

Department of Energy  
Carlsbad Field Office  
P. O. Box 3090  
Carlsbad, New Mexico 88221

JUN 09 2004



Mr. James Bearzi  
New Mexico Environment Department  
Hazardous Waste Bureau  
2905 Rodeo Park Drive East, Building 1  
Santa Fe, NM 87505-6303



Subject: Response to Observer Inquiry from Audit A-04-25

Dear Mr. Bearzi:

The New Mexico Environment Department (NMED) issued an Observer Inquiry on May 6, 2004, pertaining to the Lawrence Livermore National Laboratory (LLNL), Audit A-04-25. The Department of Energy (DOE) believes the following information provides the needed response.

In the Observer Inquiry the NMED questioned how the removal and replacement of drum filters would impact the validity of headspace gas sampling and analysis and why the drum age criteria (DAC) clock does not need to be re-started after filter change out prior to taking a subsequent headspace gas sample. The NMED requested information to indicate that the loss of volatile organic compounds (VOCs) is insignificant (i.e., less than or similar to the quantity of VOCs removed in the collection of a headspace gas sample and a duplicate sample). The NMED also requested that DOE re-evaluate the WIPP Hotline responses numbers 46, 47 and 167 in light of the Hazardous Waste Facility Permit (HWFP) in which multiple DAC scenarios exist.

In preparation for the LLNL audit, eight drums were sampled for headspace gas. The drums at LLNL use the Scenario 3, Packaging Configuration 2 default DAC of 175 days (Section B1, Table B1-9). Subsequent to sampling through the filter, new filters were emplaced per procedure CCP-TP-104, Rev. 1, *CCP Preparing and Handling Waste drums for Headspace Gas at Lawrence Livermore National Laboratory*. Due to unforeseen circumstances the traceability of the samples were compromised and new samples were required. The drums were held until the container thermal equilibrium requirement was achieved per the WAP Section B1-1a. New headspace gas samples were taken and subsequently analyzed.

During the headspace gas sampling process only the metal top on the filter (which is held on by four spot welds) is removed - the filter media remains in place. The removal of the metal plate on the top of the filter is required so that the sampling needle can be inserted into the drum headspace. The filter media remains intact during this process. After sampling, the drum is moved to a location where the filter can be replaced. The filter is unscrewed, removed and replaced. As graphically shown in Enclosure 1,



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*Lawrence Livermore Headspace Gas Sampling Processes*, the total process time needed to change a filter is less than five minutes and the time that no filter is on the drum lid is less than a minute (i.e., the change out process is continuous).

In the LLNL Observer Inquiry, the NMED stated "However, CBFO did not provide analysis to demonstrate that the VOC loss is insignificant (i.e., less than or similar to the quantity of VOCs removed in the collection of a HSG sample and a duplicate sample)." The proper criterion is to determine if there will be a significant difference in the VOC concentration from samples taken before and after replacement of the filter vent, which takes into account the quantity of VOCs lost relative to the VOCs in the container headspace. There already exists a criterion to evaluate the acceptability of VOC concentrations in duplicate samples taken from the same container that is applicable to this inquiry. The HWFP requires that field and online duplicates have a relative percent difference (RPD) of less than or equal to 25 percent (Section B1, Table B1-3). There are three separate studies that support the conclusion that the loss of VOC's during filter change out results in insignificant impacts on RPD.

The Permittees have previously performed a study to justify that replacing the filter as soon as practicable does not disturb the equilibrium of the headspace gas sufficiently to require restart of the DAC waiting period. On September 28, 2001 a HWFP modification request was submitted to the NMED entitled "*Taking Samples of Headspace Gas Through Existing Filter Vent Holes*". Included with this request was an enclosure (Attachment D), which was a test plan and data demonstrating that changes in the headspace gas concentration of the pipe overpack with the filter removed for up to 5.5 minutes were within the RPD requirements of the HWFP. The test plan and data are included with this response in the enclosure entitled *Analysis of the Affects of Filter Change on Container at the Rocky Flats Environmental Technology Site*. NMED accepted these data and subsequently approved the HWFP modification.

In addition, Lockheed Martin Idaho Technologies Company performed a study entitled: *Possible Sample Dilution From Installation of Gas-Tight Sampling Device on Vented Waste Drums – KJL-09-08, October 14, 1998*, which is enclosed with this response. This study was performed to ascertain if there was any dilution of the headspace gas when the filter on a 55-gallon drum was removed and a gas-tight seal installed. Different time periods between thirty seconds up to two minutes were evaluated where the drum lid filter vent hole was not covered. The results of the study showed insignificant (< 1.6 percent) dilution of the headspace gas in cases where the duration of opening in the drum lid was up to two minutes. The study did not consider a longer period than two minutes and is extremely conservative because it considers the effects of an air stream flowing over the open hole.

To address the NMED inquiry, additional mathematical evaluations have been performed using the following assumptions to indicate that the removal and

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replacement of a filter will not impact the headspace gas concentrations beyond what is required in the HWFP. This evaluation is included in an enclosure to this response.

The assumptions used in the evaluation were:

- The container has met the DAC (i.e., the headspace gas is at least at 90 percent of steady state)
- The VOC/drum liner equilibrium remains intact
- The VOC concentration in other void volumes do not change significantly
- The VOC rate across the confinement layers (excluding the drum lid) do not change upon removal of the filter
- The vent diameter is 11/16 inches
- The lid is 1/16 inch thick (typical drum lid thickness)
- There are 28 liters of headspace between the liner lid and the drum lid (as used in the position paper entitled *Position for Determining Gas Phase Volatile Organic Compound Concentrations in Transuranic Waste Containers, INEL-95/0109, Revision 1, Table D1*. This value was used in the VDRUM Model approved by NMED for new DACs in January 2003.)

Using the ideal gas law equation it is possible to calculate the volume in moles of VOCs that will be lost over time. These calculations are conservative as they only consider the diffusion of VOCs out of the opening and neglect the VOCs diffusing into the container headspace across the drum liner lid. Given the constant volume of the drum headspace the percentage change in the VOC moles is equivalent to the change in VOC concentration.

Based upon the previous assumptions the calculated percent of VOCs lost from the drum headspace after 5.5 minutes with no filter vent in place is 2.3 percent. Only 0.42 percent is lost in one minute. These concentration impacts are well within the 25 percent RPD required by the HWFP (Section B1, Table B1-3).

Based on the previous assumptions and the HWFP requirement that duplicate samples must have a relative percent difference (RPD) of less than or equal to 25 percent it would take at least 41 minutes for enough VOCs to leave the drum headspace to exceed the 25 percent RPD requirement.

The calculations indicate that the data obtained in the RFETS study for pipe components are valid for other containers and packaging configurations in which the DAC (equilibrium) has been met, the headspace volume sampled is comparable or larger than the pipe component volume (30 liters), and the filter is changed quickly. The impact on VOC concentration will be less significant in containers with larger headspace volume because the filter vent opening in all container lids are comparable and therefore lose similar amounts of VOCs over the same time period. VOC loss is proportional to the diameter of the filter vent hole. As a result the relative change in VOC concentration will be less in containers with larger headspace volume.

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These data are sufficient to document that there is no adverse impact on the headspace gas concentrations during the filter change-out process and that there is no need or benefit in waiting another DAC of 175 days prior to re-sampling drums. Additionally, the data demonstrates that the HWFP Data Quality Objectives specified in Section B3-2 (also Section B1, Table B1-3) are met.

Based on these conclusions, the Permittees have re-evaluated the applicability of the WIPP HOTLINE responses 46, 121 and 167 (47 does not apply to this issue) as referenced in the inquiry and other DAC related responses. The above information/data indicates that the responses are still valid and no changes are required.

If you have any additional questions regarding this matter, please contact me at (505) 234-7357.

Sincerely,



Kerry W. Watson  
CBFO Assistant Manager  
Office of National TRU Program

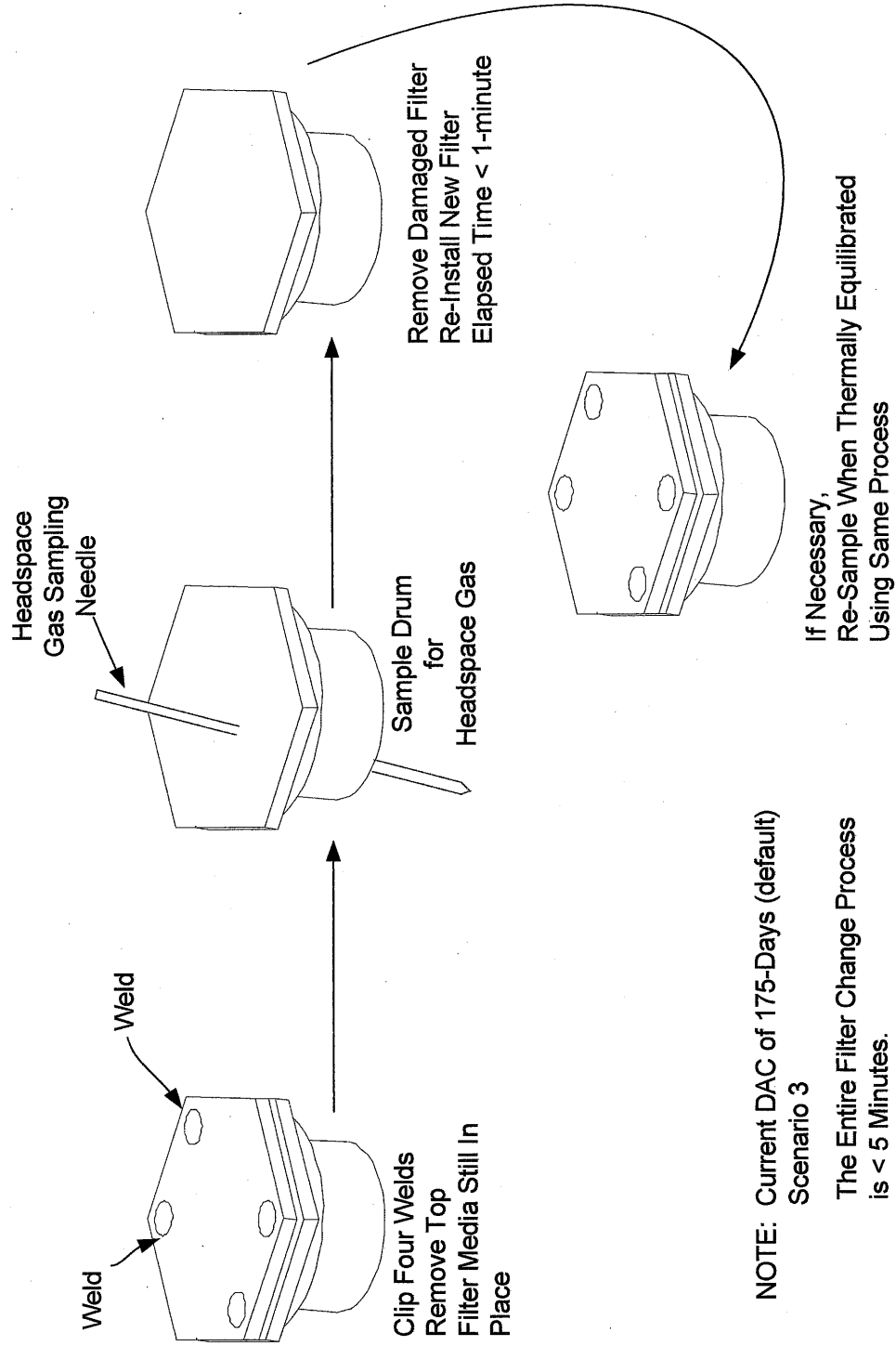
Enclosure

cc: w/enclosure  
R. Knerr, CBFO  
R. McCallister, CBFO  
A. Holland, CBFO  
S. Zappe, NMED  
CBFO M&RC

## Enclosure 1

### Lawrence Livermore Headspace Gas Sampling Processes

# Lawrence Livermore Headspace Gas Sampling Process



NOTE: Current DAC of 175-Days (default)

Scenario 3

The Entire Filter Change Process  
is < 5 Minutes.

## Enclosure 2

### Test Plan

Evaluation of Gas Tight Seal for Collection of Headspace Gas Samples from  
Pipe Overpack Components

TEST PLAN  
EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM  
PIPE OVERPACK COMPONENTS

Summary:

An empty Pipe Overpack Component (POC) will be evacuated and filled with a reference standard (i.e., with the field reference standard) with known concentrations of seven volatile organic compounds (VOCs) (see Table 1) using a gas tight seal connection between a sampling manifold that is equipped with sampling canisters, a reference standard and a vacuum pump. The gas inside the POC will be evacuated and replaced with the reference standard gas. A baseline gas sample will be taken just prior to removal and replacement of the gas tight seal on the POC. A test headspace gas sample will be collected from inside the POC immediately after removal/replacement of the gas tight seal. The samples will be analyzed for headspace gas VOCs. The results from the baseline sample will be compared to the results from the test headspace gas sample and the results from these two samples will be compared with the standard values for the reference standard to determine if there is any significant difference between any of them. The test will be repeated several times to evaluate the effect of increasing the time duration that the POC headspace is exposed to room atmosphere.

Table 1  
Known Concentration of VOCs in Reference Standard

VOC Name	Standard Value (ppmv)
Benzene	12.2
cis-1,2-Dichloroethylene	12.0
1,1-Dichloroethane	12.1
1,2-Dichloroethane	12.1
1,1-Dichloroethene	12.3
Tetrachloroethylene	12.2
1,1,1-Trichloroethane	12.0

Purpose:

Testing will evaluate effects on headspace gas VOC concentrations when collecting samples utilizing the gas tight seal sampling methodology. Using the gas tight seal involves opening the drum to expose the top of the POC itself, removing the POC filter and replacing it with a gas tight seal, and drawing a gas sample from the POC through the gas tight seal into a Summa canister. Using this method, a concern has developed that some of the VOCs in the headspace of the POC could escape while the POC filter is exchanged for the gas tight seal, thereby compromising the sample integrity and representativeness. The purpose of this test plan is to evaluate this concern to determine if there is any significant loss of VOCs in the execution of this sampling methodology.

Hypothesis:

There is no difference between the actual gas concentration of VOCs inside a Pipe Overpack Component (POC) and corresponding concentrations in a headspace sample of this same gas collected using the gas tight seal sampling method (i.e., removing the POC filter/plug and installing a gas tight seal to collect the sample).

Reviewed For CI: NI  
By: William Delmont  
Date: 22 AUG 01 KAM  
CEX-073-75

TEST PLAN  
EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM  
PIPE OVERPACK COMPONENTS



**Procedure:**

The following steps outline the general procedure to be followed in the execution of this test plan. All headspace sampling, and sample handling, custody, traceability and analysis procedures will be followed during the execution of this test plan.

1. Obtain an empty POC drum and remove the drum lid and associated packaging to expose the lid of the POC.
2. Remove the filter from the POC filter port and attach a gas tight seal that is connected to a sampling manifold equipped with sampling canisters, a vacuum pump and a field reference standard cylinder.
3. Evacuate the POC using the vacuum pump to a pressure of approximately 100 microns of mercury.
4. Perform a rate of rise leak test on the POC. Evacuation and sealing is considered adequate when the rate of rise is less than 5 microns per second.
5. Record the atmospheric pressure, the final POC evacuation pressure (that also corresponds to the initial rate of rise pressure), the final rate of rise pressure, the time interval between the initial and final rate of rise pressures and the calculated rate of rise.
6. Isolate the vacuum pump from the sampling manifold/POC and then slowly add field reference standard through the manifold into the POC.
7. Pressurize the POC with field reference standard to 10 torr or greater above atmospheric pressure. Record this pressure.
8. Isolate the field reference standard from the sampling manifold/POC.
9. Allow the gas inside the POC and manifold to equilibrate for approximately 15 minutes. Record this equilibration time.
10. Withdraw a baseline gas sample into a clean Summa canister from the combined manifold/POC system and record the system pressure after sample collection. This pressure must be greater than atmospheric pressure.
11. Vent the combined manifold/POC system through the manifold to equalize the pressure inside the POC with atmospheric pressure.
12. The following steps are to be performed as they would be performed when actually headspace sampling a POC in accordance with procedure L-4146, Headspace Gas Sampling of Waste Containers:
  - a. Remove the manifold gas tight seal from the POC. (This step is identical to removing the POC filter when executing procedure L-4146.)
  - b. Connect a different manifold gas tight seal to the POC. (This step is identical to attaching the gas tight seal to the POC when executing procedure L-4146.)
  - c. Record the POC exposure time (i.e., the time the POC was not equipped with a gas tight seal).
  - d. Collect a test headspace gas sample from the POC headspace.
  - e. Record the pressure of the manifold/POC system after sample collection.
13. Without removing or changing the gas tight seal, refill the manifold/POC system with field reference standard to 10 torr or greater above atmospheric pressure. Record this pressure.
14. Repeat steps 8 through 13.
15. Analyze all headspace gas samples per WIPP approved procedures.

The POC exposure time will be actually measured in the initial tests to establish a baseline that estimates the time it takes to remove and replace the POC filter with a gas tight seal under routine headspace gas sampling operations. In addition, tests will also be performed at measured exposure times that exceed this average routine time. The specific tests and associated exposure times are presented in Table 2:

**TEST PLAN**  
**EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM**  
**PIPE OVERPACK COMPONENTS**

Table 2  
POC Exposure Times to be Evaluated

Test Number	POC Exposure Time (minutes)
1	As measured
2	As measured
3	As measured
4	Average as measured time plus 0.5 minutes
5	Average as measured time plus 1 minute
6	Average as measured time plus 2 minutes
7	Average as measured time plus 5 minutes

**Use of Results:**

Results from each of the baseline samples will be compared with results from the corresponding test POC headspace sample and a relative percent difference (RPD) will be calculated. If the RPD for a pair of samples is less than or equal to 25 % then the two samples satisfy the field quality control sample acceptance criteria for field duplicates. This is interpreted to mean that there is no significant difference, based on the WIPP Hazardous Waste Facility Waste Analysis Plan (WAP), between the two samples. If the samples do not satisfy the RPD criterion, then this will be interpreted to mean that there is a significant difference, based on the WIPP WAP, between the two samples.

Additionally, the results from both the baseline sample and the test POC headspace sample will be compared to the standard values for the field reference standard. If the percent recovery (%R) is between 70 to 130 % for all six analytes, then a sample satisfies the field quality control sample acceptance criteria for field reference standards. This will be interpreted to mean that there is no significant difference, based on the WIPP WAP, between the field reference standard and the sample analyzed. If the %R is not between 70 to 130 % for all six analytes, then a sample does not satisfy the field quality control sample acceptance criteria for field reference standards. This will be interpreted to mean that there is a significant difference, based on the WIPP WAP, between the field reference standard and the sample analyzed.

**Concurrence:**

  
\_\_\_\_\_  
G. A. O'Leary, Manager, TRU Waste Programs

8/16/01  
\_\_\_\_\_  
Date

TEST PLAN  
EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM  
PIPE OVERPACK COMPONENTS

August 16, 2001

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## TEST RESULTS

Results from the execution of the Test Plan for the Evaluation of Gas Tight Seal for Collection of Headspace Gas Samples from Pipe Overpack Components are summarized in Table 1. The results are presented in order of the seven tests that are specified in the Test Plan. For each test, the analysis results for the seven reference standard volatile organic compounds (VOCs) are reported for both the baseline sample and the test sample along with the evaluated exposure time (i.e., the time while the Pipe Overpack Component (POC) vent port was not equipped with a gas tight seal). For each baseline and test sample, the percent recovery (%R) was calculated for each of the seven VOCs and compared to the acceptance criteria for field reference standards given in the WIPP Hazardous Waste Facility Waste Analysis Plan (WAP), Table B1-3. The formula used to calculate the %R is given in Section B3-1 of the WAP (equation B3-5). If the VOC recovery satisfied the acceptance criteria then it is designated as "Pass." If the VOC recovery did not satisfy the acceptance criteria, the VOC is designated as "Fail." Additionally, the results for each of the seven VOCs from the baseline sample were compared with the corresponding results from the test sample by calculating the relative percent difference (RPD) using equation B3-1 presented in Section B3-1 of the WAP. The calculated RPD was then compared to the acceptance criteria for field duplicates specified in the WAP, Table B1-3. Again, if the VOC RPD satisfied the acceptance criteria then it is designated as "Pass" while if it did not satisfy the acceptance criterion it is designated as "Fail."

From the results given in Table 1, no VOC in any of the seven tests failed any of the criteria (%R or RPD). Exposure times ranged from 28 seconds (0.47 minutes) to 329 seconds (5.48 minutes). Therefore, the conclusion of the test is that there is no significant difference, based on the WIPP WAP, between the baseline sample and the corresponding test sample or between the standard values of the reference standard used and either the baseline sample results or the test sample results over the range of exposure times tested. From the results of the subject test plan, sampling of a POC using a gas tight seal does not significantly bias the VOC composition of the headspace gas sample with respect to the VOC composition of the headspace gas itself inside of the POC.

Reviewed For Classification/UCNI  
By W. J. Delaney  
Date 22 AUG 01 (KAM)  
CEX-073-95

Table 1

# TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS

## Test 1

Exposure Time: 40 seconds (0.67 minutes)

Baseline Sample ID: 01W7538

Test Sample ID: 01W7539

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample			Test Sample			Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Acceptance Criteria
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0 <=25
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108.7	70 to 130 %	Pass	7.4 <=25
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	13	107.7	70 to 130 %	Pass	7.4 <=25
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0 <=25
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	12	97.6	70 to 130 %	Pass	8.0 <=25
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	8.7 <=25
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108.7	70 to 130 %	Pass	0.0 <=25

## Test 2

Exposure Time: 31 seconds (0.52 minutes)

Baseline Sample ID: 01W7540

Test Sample ID: 01W7541

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample			Test Sample			Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Acceptance Criteria
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0 <=25
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108.7	70 to 130 %	Pass	7.4 <=25
1,1-Dichloroethane	12.1	15	124.0	70 to 130 %	Pass	14	116.7	70 to 130 %	Pass	6.9 <=25
1,2-Dichloroethane	12.1	13	107.4	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	8.0 <=25
1,1-Dichloroethene	12.3	14	113.8	70 to 130 %	Pass	13	106.7	70 to 130 %	Pass	7.4 <=25
Tetrachloroethylene	12.2	11	90.2	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	0.0 <=25
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108.7	70 to 130 %	Pass	0.0 <=25

Table 1

**TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS**

**Test 3**

Exposure Time: 28 seconds (0.47 minutes)

Baseline Sample ID: 01W7598

Test Sample ID: 01W7588

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	13	108.70	to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116.70	to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	13	106.70	to 130 %	Pass	0.0	<=25	Pass
Tetrachloroethylene	12.2	11	90.2	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108.70	to 130 %	Pass	0.0	<=25	Pass

**Test 4**

Exposure Time: 62 seconds (1.03 minutes)

Baseline Sample ID: 01W7599

Test Sample ID: 01W7597

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	12	98.4	70 to 130 %	Pass	12	98.4	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	14	116.7	70 to 130 %	Pass	13	108.70	to 130 %	Pass	7.4	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116.70	to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	12	99.2	70 to 130 %	Pass	12	99.2	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	12	97.6	70 to 130 %	Pass	8.0	<=25	Pass
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	11	90.2	70 to 130 %	Pass	8.7	<=25	Pass
1,1,1-Trichloroethane	12	13	108.3	70 to 130 %	Pass	13	108.70	to 130 %	Pass	0.0	<=25	Pass

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Table 1

**TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS**

**Test 5**

Exposure Time: 89 seconds (1.48 minutes)

Baseline Sample ID: 01W7587

Test Sample ID: 01W7591

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	14	114.8	70 to 130 %	Pass	13	107.7	70 to 130 %	Pass	7.4	<=25	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	12	100.7	70 to 130 %	Pass	8.0	<=25	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116.7	70 to 130 %	Pass	0.0	<=25	Pass
1,2-Dichloroethane	12.1	11	90.9	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	0.0	<=25	Pass
1,1-Dichloroethene	12.3	14	113.8	70 to 130 %	Pass	13	106.7	70 to 130 %	Pass	7.4	<=25	Pass
Tetrachloroethylene	12.2	12	98.4	70 to 130 %	Pass	9.6	78.7	70 to 130 %	Pass	22.2	<=25	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	11	91.7	70 to 130 %	Pass	8.7	<=25	Pass

**Test 6**

Exposure Time: 162 seconds (2.70 minutes)

Baseline Sample ID: 01W7593

Test Sample ID: 01W7596

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison		
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail
Benzene	12.2	13	106.8	70 to 130 %	Pass	13	107.7	70 to 130 %	Pass	0.0	<=25	Pass
cis-1,2-Dichloroethylene	12	12	100.0	70 to 130 %	Pass	13	108.7	70 to 130 %	Pass	8.0	<=25	Pass
1,1-Dichloroethane	12.1	13	107.4	70 to 130 %	Pass	14	116.7	70 to 130 %	Pass	7.4	<=25	Pass
1,2-Dichloroethane	12.1	10	82.6	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	9.5	<=25	Pass
1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	14	114.7	70 to 130 %	Pass	7.4	<=25	Pass
Tetrachloroethylene	12.2	9.8	80.3	70 to 130 %	Pass	9.5	77.9	70 to 130 %	Pass	3.1	<=25	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	11	91.7	70 to 130 %	Pass	8.7	<=25	Pass

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Table 1

**TEST PLAN FOR THE EVALUATION OF GAS TIGHT SEAL FOR COLLECTION OF HEADSPACE GAS SAMPLES FROM PIPE OVERPACK COMPONENTS**

**RESULTS SUMMARY FROM**

Test 7

Exposure Time: 328 seconds (5.48 minutes)

Baseline Sample ID: 01W7589

Test Sample ID: 01W7590

Atmospheric Pressure: 618.7 torr

Analyte	Standard Value (ppmv)	Baseline Sample				Test Sample				Baseline/Test Sample Comparison			
		Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	Results (ppmv)	%R	Acceptance Criteria	Pass/Fail	RPD	Acceptance Criteria	Pass/Fail	Pass/Fail
Benzene	12.2	13	106.6	70 to 130 %	Pass	13	107	70 to 130 %	Pass	0.0	<=25	Pass	Pass
cis-1,2-Dichloroethylene	12	13	108.3	70 to 130 %	Pass	13	108	70 to 130 %	Pass	0.0	<=25	Pass	Pass
1,1-Dichloroethane	12.1	14	115.7	70 to 130 %	Pass	14	116	70 to 130 %	Pass	0.0	<=25	Pass	Pass
1,2-Dichloroethane	12.1	11	90.9	70 to 130 %	Pass	11	90.9	70 to 130 %	Pass	0.0	<=25	Pass	Pass
1,1,1-Dichloroethene	12.3	13	105.7	70 to 130 %	Pass	13	106	70 to 130 %	Pass	0.0	<=25	Pass	Pass
Tetrachloroethylene	12.2	9.1	74.6	70 to 130 %	Pass	9.5	77.9	70 to 130 %	Pass	4.3	<=25	Pass	Pass
1,1,1-Trichloroethane	12	12	100.0	70 to 130 %	Pass	12	100	70 to 130 %	Pass	0.0	<=25	Pass	Pass



Enclosure 3

Possible Sample Dilution for Installation of Gas-Tight Sampling Device on Vented  
Waste Drums and Associated Correspondence

## Lockheed Martin Idaho Technologies Company

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INTERDEPARTMENTAL COMMUNICATION

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Date: October 14, 1998

To: R. E. Arbon, MS 4201

From: K. J. Liekhus, MS 3625 *KJL*

Subject: POSSIBLE SAMPLE DILUTION FROM INSTALLATION OF GAS-TIGHT SAMPLING DEVICE ON VENTED WASTE DRUMS - KJL-09-98

- References:
- 1) R. E. Arbon, 1997, "Headspace Sampling Using the Gas Tight Seal," Function File Number INEEL/INT-97-013333, EDF Serial Number-RWMC-1000.
  - 2) K. J. Liekhus, 1995, Characterization of Void Volume VOC Concentration in Vented TRU Waste Drum - Final Report, INEL-94/0252, Lockheed Idaho, Idaho Falls, ID.

In an effort to improve gas sampling of the headspace of vented waste drum as indicated by the relative percent difference (RPD) by sample duplicates, a sampling method has been developed that uses a gas tight seal and preset sampling needle [Reference 1]. The sampling apparatus is installed in the drum lid after removing the drum vent. The issue has been raised that this particular step of installing the sampling apparatus provides a means for air to easily enter the drum headspace and dilute the resulting gas sample. This letter summarizes detailed analysis that shows that this concern is not warranted.

Air can enter the drum by convection (flow conditions) or by diffusion. If the pressure differential across the drum fluctuates, the resulting breathing of the drum will draw air in by convection. If gas flow out of the drum is not significant, air will diffuse into the drum as the drum gas diffuses out. Each case will be examined to determine the potential impact on any gas sample collected from the drum headspace.

In order to prevent the release of any radioactive particulates when the drum vent is removed, a trapezoidal funnel attached to a vacuum line was placed adjacent to the opening in the drum lid. The vacuum pulled a stream of air into the funnel and across a high-efficiency particulate air (HEPA) filter. The average volumetric flow rate across the funnel opening was measured to be approximately 100 actual cubic feet per minute. The cross sectional area of the funnel opening is 0.45 ft<sup>2</sup>.

It is possible that the airflow across the opening is sufficient to create a pressure differential that will promote gas flow out of the drum. Using Bernoulli's equation, the pressure above the opening in the drum lid,  $p_2$ , was estimated to be

-----

$$p_2 = p_1 - \frac{v_2^2}{2g_c} \quad (1)$$

where

- $p_1$  - ambient pressure at point a significant distance from drum lid opening  
 $v_2$  - gas velocity across drum lid opening,  $\text{ft s}^{-1}$   
 $g_c$  - constant =  $32.2 \text{ lb}_m \text{ ft lb}_f^{-1} \text{ s}^{-2}$

It is assumed that the gas velocity at the point where the ambient pressure was measured is zero. The linear velocity of air across the opening is assumed to equal the linear velocity air at the face of the funnel. This was estimated to be  $3.7 \text{ ft s}^{-1}$ . The resulting pressure drop was calculated to be 0.04 in. water gage (w. g.) or  $9 \times 10^{-5} \text{ atm}$ . The total volume of gas removed from the drum if the pressure in the drum was decreased by 0.04 in. w. g., assuming total void volume of 30 L. is 3 mL. Despite the withdrawal of gas resulting from a pressure drop across the drum lid, the gas inside the drum is not diluted until air is allowed to enter the drum. If the vacuum sweep remains on, air entry via convection should not occur.

A more likely scenario for air intrusion into the drum is by diffusion. The vacuum sweep assures that the gas concentration outside the drum equals zero. The gas diffusion rate of species  $i$ ,  $R_i$ , across the opening in the drum lid upon removal of the drum vent is defined as

$$R_i = D_i A \frac{\Delta c_i}{\Delta x} \quad (2)$$

where

- $D_i$  - diffusivity of species  $i$ ,  $\text{cm}^2 \text{ s}^{-1}$   
 $A$  - cross-sectional area of opening,  $\text{cm}^2$   
 $c_i$  - concentration of species  $i$ ,  $\text{mol cm}^{-3}$   
 $\Delta x$  - diffusion length, cm

The cross-sectional area of the hole in the drum lid is approximately  $0.7 \text{ cm}^2$ , the same as for the drum liner. Earlier models of diffusion across the drum liner lid [Reference 2] showed that, in the case where uniform gas composition is assumed in each layer of confinement, a diffusion length greater than the thickness of the lid exists between the bulk gases on both sides. This reflects the gradients that develop across the opening. The same principle applies to the drum lid with the drum vent removed. The diffusion length across the drum lid without a vacuum sweep has not been characterized but I assumed it to be equivalent to that determined for the drum liner lid which is 1.4 cm [Reference 2]. A conservative assumption is that the presence of the vacuum sweep effectively cuts the diffusion length in half to 0.7 cm. Gas diffusivity is on the order of  $0.1 \text{ cm}^2 \text{ s}^{-1}$  at room temperature and pressure. The gas concentration of species  $i$  is defined as

$$c_i = y_i c$$

(3)

where

$y_i$  - mole fraction of species  $i$   
 $c$  - total gas concentration in drum =  $P/RT$   
 $P$  - gas pressure  
 $R$  - gas constant  
 $T$  - absolute gas temperature

At a temperature of 298 K and ambient pressure of 0.85 atm, the gas concentration in the drum is  $3.5 \times 10^{-3}$  mol  $\text{cm}^{-3}$ . The diffusion rate is calculated to be  $3.5 \times 10^{-6}$   $y_i$  mol  $\text{s}^{-1}$ . This rate is assumed to be constant for the brief time period being considered. The moles of species  $i$  that diffuse out the drum and are replaced by air equal the product of the diffusion rate calculated above and the total time the opening is uncovered.

During drum sampling, approximately 750 mL of gas is withdrawn with the last 250 mL being direct to an evacuated Summa canister. The total number of moles of species  $i$  in 750 mL of gas is  $2.6 \times 10^{-2}$   $y_i$  mol. The percentage of species  $i$  replaced by air in 250 mL was calculated for different time periods in which the opening in the drum lid was not covered with a drum vent or gas sampling device:

30 sec: $(30 \text{ s})(3.5 \times 10^{-6} y_i \text{ mol s}^{-1})(100)/(2.6 \times 10^{-2} y_i \text{ mol})$	= 0.4 %
60 sec:	= 0.8 %
90 sec:	= 1.2 %
120 sec:	= 1.6 %

The analysis of all likely pathways for air penetration into the drum during the removal of the drum vent and installation of a gas-tight sampling device indicate that no significant dilution of the gas sample should occur. In addition, it is highly likely that the air that diffuses into the drum will be contained in the approximately 500 mL of sample used to purge the sample lines.

I conclude that the gas volume within a vented waste will not be significantly diluted by air during the removal of a drum vent and installation of a gas sampling device if the time the opening in the drum lid is left exposed is no greater than 2 minutes.

blm

cc: T. L. Clements, MS 4201  
G. Hayes, MS 4202  
E. Dumas, MS 4201  
R. E. Evans, MS 4107  
Project File  
K. J. Liekhus Letter File

Project File Number N/A

Project/Task Headspace Sampling

Subtask \_\_\_\_\_

**ORIGINAL - RED**  
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Title: Headspace Sampling Using the Gas Tight Seal

**Summary:** This EDF outlines the use of a gas tight seal which has proven to significantly improve precision during the collection of transuranic waste drum headspace samples. In addition this EDF documents the precision data taken with the gas tight seal and demonstrates that the gas tight seal meets all of the requirements given in Procedure 110.3 of the WIPP Sampling and Analysis Methods Manual. When the Radioactive Waste Management Complex (RWMC) sample manifold is not used, headspace samples will be collected using the gas tight seal.

**Introduction:**

To characterize the headspace gas of retrievably stored transuranic (TRU) waste in accordance with the Transuranic Waste Characterization Program (TWCP) Quality Assurance Program Plan (QAPP) the precision for both the sampling method and the analytical methods must be evaluated and a minimum of 25% relative percent difference (RPD) between duplicates achieved. At the Idaho National Engineering and Environmental Laboratory (INEEL) the analytical methods are consistently within the precision requirements while the precision associated with the sampling methods have periodically been outside of the QAPP established RPD limit. The TWCP INEEL Site Project Office (SPO) reviewed existing headspace field duplicate RPD values and documented their findings in engineering design file (EDF) RWMC-810. The conclusion of this review was that existing manual field sampling methods, with the notable exception of the sampling manifold, are outside of the QAPP required levels 30% to 43% of the time.

In an effort to improve manual sampling RPD values SPO and Environmental Chemistry Laboratory (ECL) personnel reviewed potential causes of nonconforming duplicate precision. A number of parameters were thoroughly reviewed with the most probable causes being the lack of a gas tight seal and improper needle orientation during sample collection. A drum filter, shown in Figure 1 (attached), capable of achieving a gas tight seal and eliminating the difficulty in achieving proper needle orientation was developed at the ECL and tested at the Radioactive Waste Management Complex (RWMC). Seven duplicate sets were taken using the gas tight seal from a content code three drum. The samples were analyzed at the ECL and the results are given in Table 1 (attached). All of the RPD values are in compliance with QAPP precision requirements. This is a significant improvement in the RPD failure rate. When the RWMC sample manifold is not used, the gas tight seal described in this EDF will be the manual headspace sampling technique employed at the RWMC. Finally the gas tight seal meets the requirements outlined in Procedure 110.3 of the Transuranic Waste Characterization Sampling and Analysis Method Manual (SAMM) and can be implemented immediately.

Project File Number N/A

#### Experimental:

The gas tight seal is composed of a compact in-line 0.5  $\mu$ m sintered stainless steel filter and 1/16" side port needle connected to a threaded drum filter housing assembly via a 1/4" x 1/16" swagelock reducing union. A breakdown of the gas seal components is given in Figure 1 Detail A. A gas tight seal is provided by the reducing union around the needle. The 1/16" side port needle extends into the headspace of the drum consistent with Procedure 110.3 TWCP SAMM. Use of the gas tight seal is achieved by removing the carbon composite filter and replacing with the gas tight seal. Care should be taken to perform filter replacement within approximately one minute. When properly installed the housing assembly has a interface seal gasket which ensures a gas tight seal against the drum.

Because of the consistent presence of volatile organic compounds greater than the program required quantitation limit a content code three drum was selected for sampling with the gas tight seal. RWMC operations personnel connected a sample pump to the gas tight seal and collected the samples into a summa canisters sequentially. One duplicate sample set was collected daily for five days. The remaining two duplicate sets were taken in the morning and afternoon of the sixth day. The resulting headspace gas samples were then analyzed at the ECL following WIPP QAPP protocol.

#### Results and Discussion:

Review of the existing sampling methods in EDF-810 indicated that the direct summa sampling, tee connection sampling, and use of the sampling pump have been unsuccessful in eliminating duplicate RPD problems. Two critical steps, proper orientation of the side port needle and use of an elastomer film, are common to each method. To successfully collect a headspace sample using the above methods a 6-inch square sheet of elastomer film is folded in half twice and placed on top of the carbon composite filter. An o-ring is then placed over the film and carbon composite filter. The needle is then pressed through the film and carbon composite filter. During this process it is crucial that the elastomer be sealed gas tight and that the needle is completely inserted through the filter housing and into the headspace of the drum. If not properly performed the integrity of the sample collected is compromised. In tests conducted by SPO personnel inserting the needle completely through the carbon composite filter was not a trivial task. Many times the needle wedged against the inner wall of the filter housing. To help simplify and improve the sampling process the gas tight seal was developed and tested.

As shown in Table 1 all of the samples collected with the gas tight seal were within QAPP parameters for the analyte carbon tetrachloride. Other analytes present in the headspace behaved similarly and were within the 25% limit. Given the failure rate outlined in EDF RWMC-810, two to three of the duplicates would have been expected to have been outside of QAPP requirements. Thus it is reasonable to assume that eliminating the uncertainty in needle orientation and use of the elastomer film by the replacement with the gas tight seal significantly improves the precision of headspace sampling. It should be pointed out that the samples were taken by RWMC personnel. No special precautions were taken in the collection of the precision test samples.

Project File Number N/A

Collection of headspace samples, described in detail in the experimental section, with the gas tight seal is consistent with both Procedure 110.2 and Procedure 110.3. The sintered stainless steel filter and sideport needle are identical to the filter used in Procedure 110.2 and 110.3. However, unlike sample collection using SAMM Procedures 110.2 and 110.3, a true gas tight seal and proper position of the needle is insured by the design. The side port needle is sealed gas tight using a swage lock fitting. In addition this eliminates the depth uncertainty associated with inserting the needle through the carbon composite filter. The depth is identical each time. The sealing surface between the drum and the housing assembly is gas tight as well. The housing is threaded tightly against the drum lid ensuring a gas tight seal between the housing rubber surface and drum. Diffusion of air into the drum during the replacement of the carbon composite filter is negligible. Diffusion calculations have demonstrated that the sample is diluted 0.6% or less.

**Conclusion:**

When the RWMC sample manifold is not used headspace samples will be collected using the gas tight seal. Collection of samples using this process is consistent with both SAMM Procedure 110.2 and Procedure 110.3 and can be implemented immediately.

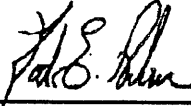


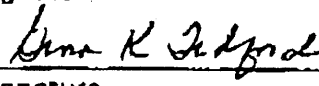


**Attachments:**

Attachment 1: Figure 1, Engineered Gas Seal

Attachment 2: Table 1, RWMC Drum Headspace Sampling Replicate Precision Test Analysis

Distribution (complete package):

Distribution (summary package only):

Author: R. E. Arbon Site Project Manager	Date 11/20/97	Signature 
Reviewed: R. Evans, Tech. Review	Date 11/25/97	Signature 
Reviewed: E. Dumas, QA Review	Date 11/20/97	Signature 
Reviewed: G. Tedford, Operations	Date 11/25/97	Signature 
LMITCO Review: B. Ford, 3100 m <sup>3</sup> Project Manager	Date 12/10/97	Signature  for B. K. Ford
LMITCO Approval: T. Clements, TRU Waste Program Manager	Date 12/18/97	Signature 

See Management Control Procedure (MCP) 6 for instructions on use of this form.



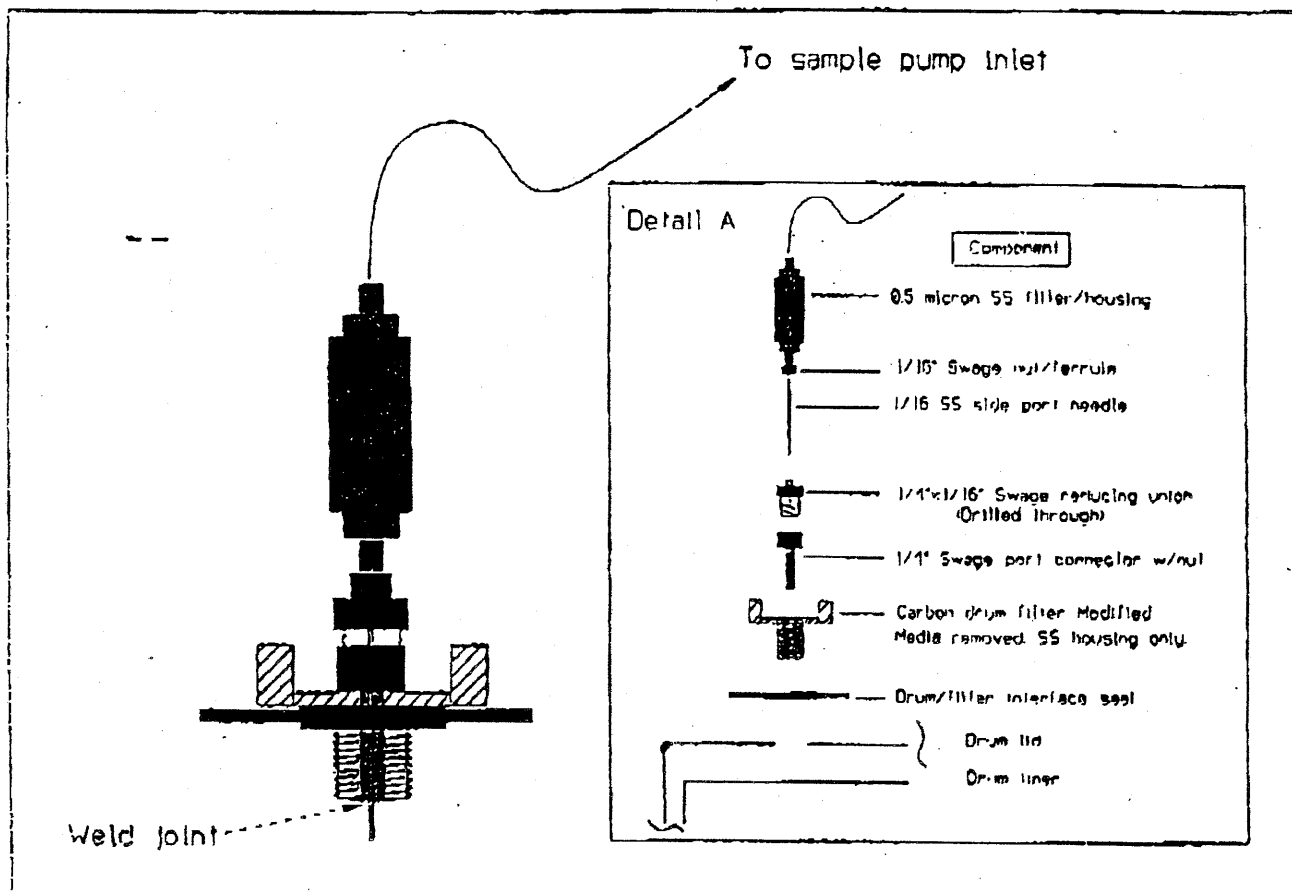


Figure 1. Engineered Gas Seal

Table 1. RWMC Drum Headspace Sampling Replicate Precision Test Analysis

Analyte	Measured Value						
	Sample Set No.						
	1	2	3	4	5	6	7
Carbon	PPMV	PPMV	PPMV	PPMV	PPMV	PPMV	PPMV
Tetrachloride							
CANISTER 1	40165	38791	43037	36229	24195	31743	29266
CANISTER 2	35212	43919	35633	32788	21688	29052	25415
%RPD	13.14	12.40	18.82	9.97	10.93	8.85	14.09

\* Sampled on the same day (AM-PM)

Notes:

Samples collected in 250 ml 'Summa' canisters using 'gas tight' seals.

Replicate samples were collected sequentially using sampling pump. ~750 ml headspace removed for each sample.

Enclosure 4



By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling? Sheet No. 1 of 7  
 Chkd. By \_\_\_\_\_ Date \_\_\_\_\_ Proj. No. 844137.01.01.00.00

## Purpose

Waste drums characterized at Lawrence Livermore National Laboratory (LLNL) are being prepared for shipment to the Waste Isolation Pilot Plant. The drums were originally sampled after meeting their drum age criterion (DAC), a minimum waiting period. The sampling method requires that the weld top of the filter vent is removed to allow a sampling syringe to be inserted into the drum headspace. After the sample was taken, the entire filter vent housing was removed, and a new filter vent was installed. During this time, there was a small opening in the drum lid when there was no filter vent in the drum lid. In some cases, it was discovered that the volatile organic compound (VOC) concentration could not be determined from the initial sample, and another gas sample was taken at a later time. The time between samples was considerably less than the DAC duration (175 days).

The New Mexico Environmental Department (NMED) issued an Observer Inquiry on May 6, 2004 in which it expressed concern regarding the manner in which gas sampling data were obtained. In particular that:

“..CBFO [Carlsbad Field Office] did not provide analysis to demonstrate that the volatile loss is insignificant (i.e., less than or similar to the quantity of volatiles removed in the collection of a HSG [headspace gas] sample and a duplicate sample”.

This calculation brief documents the calculations that demonstrate that a representative gas sample can be taken from a waste drum after replacing its filter vent (as performed at LLNL) without requiring a waiting period equal to the DAC. This is demonstrated by use of theoretical consideration of gas diffusion across the opening as well as test data pertaining to a similar system configuration.

## Background

The LLNL containers are 55-gallon drums in which a filter vent was secured to the drum lid. The rate of VOC across the opening in the drum when the filter vent is removed is defined by the equation:

$$R_{\text{VOC,out}} = y_{\text{VOC}} \left( \frac{D_{\text{VOC}} A_{\text{open}}}{x_{\text{open}}} \right) c \quad (1)$$

where,

- $D_{\text{VOC}}$  = VOC diffusivity in air,  $\text{cm}^2 \text{s}^{-1}$
- $A_{\text{open}}$  = cross-sectional area of opening,  $\text{cm}^2$
- $x_{\text{open}}$  = lid thickness at opening, cm
- $y_{\text{VOC}}$  = VOC mol fraction in drum (assume  $y_{\text{VOC}} = 0$  outside drum)
- $c$  = Total gas concentration in drum,  $\text{mol cm}^{-3}$

For the purpose of calculating the maximum release rate, it is assumed that the VOC concentration,  $y_{\text{VOC}}$ , does not decrease while the filter vent is off the lid. The total moles of VOCs,  $N_{\text{VOC}}$ , that escape the drum headspace



By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling?

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while the filter vent is removed for a period of  $t_{\text{vent}}$  equal

$$N_{\text{VOC}} = R_{\text{VOC,out}} t_{\text{vent}} \quad (2)$$

This amount can be compared to the total number of moles of VOC in the waste drum at the time,  $N_{\text{VOC,tot}}$ , as defined by the ideal gas law:

$$N_{\text{VOC,tot}} = y_{\text{voc}} \frac{PV}{RT} \quad (3)$$

where,

$$P = 1 \text{ atm}$$

$$V = 28,000 \text{ cm}^3 \text{ for the space between the drum liner and drum (Reference 5)}$$

$$R = 82.06 \text{ (cm}^3 \text{ atm)/(mol K)}$$

$$T = 70^\circ\text{F (294.3 K)}$$

A test plan and analyses of the affects of a filter change on pipe overpack containers at the Rocky Flats Environmental Technology Site (RFETS) was conducted in 2001 (Reference 1). The test investigated whether statistically equivalent samples (less than 25% relative percent difference [RPD]) could be achieved between a gas sample collected with a filter vent on a pipe overpack and a time period after the filter vent was removed for a duration up to 5.5 minutes. It was concluded that in all tests conducted for all time periods ranging from 30 seconds to 5.5 minutes that the RPD was less than 25%.

## Results

Three questions were posed:

1. How much VOC loss can occur when the filter vent is removed for a period of 5.5 minutes, 1 minute?
2. How long after the filter vent has been removed would it take for the VOC concentration to be 75% of the steady-state VOC concentration in the drum headspace?
3. How does the model prediction of change in VOC concentrations during filter vent removal from a 55-gallon drum compare to test results for a similar container configuration and sampling scenario?

### Question 1:

How much VOC loss occurs in 5.5 minutes, 1 minute?

The release rate out of a drum, across the filter vent opening is defined by Equation 1. The parameter values are defined as follows.

A conservative VOC diffusivity is obtained from methanol which has the largest value for the ratio of its diffusivity ( $D_{\text{MeOH}}$ ) to the diffusivity of hydrogen ( $D_{\text{H}_2}$ ) in air (Reference 2).



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$$\frac{D_{\text{MeOH}}}{D_{\text{H}_2}} = 0.168$$

Hydrogen diffusivity in air is estimated by the following equation (Reference 3, p 505).

$$D_{\text{H}_2} = \frac{2.745 \times 10^{-4}}{P} \left( \frac{T}{\sqrt{T_{\text{c,H}_2} T_{\text{c,air}}}} \right)^{1.823} (P_{\text{c,H}_2} P_{\text{c,air}})^{1/3} (T_{\text{c,H}_2} T_{\text{c,air}})^{5/12} \left( \frac{1}{M_{\text{H}_2}} + \frac{1}{M_{\text{air}}} \right)^{1/2} \quad (6)$$

where

$T_{\text{c,i}}$  critical temperature of component i, K  
 $P_{\text{c,i}}$  critical pressure of component i, atm  
 $M_i$  molecular weight of component i, gram (gram mole)<sup>-1</sup>

For hydrogen (Reference 3, Table B-1):

$T_{\text{c}} = 33.3 \text{ K}$        $P_{\text{c}} = 12.80 \text{ atm}$        $M_i = 2.016 \text{ g (g mole)}^{-1}$

For air (Reference 3, Table B-1):

$T_{\text{c}} = 132 \text{ K}$        $P_{\text{c}} = 36.4 \text{ atm}$        $M_i = 28.97 \text{ g (g mole)}^{-1}$

At values of  $T = 298.15 \text{ K}$  and  $P = 1 \text{ atm}$ , then

$$D_{\text{H}_2} = \frac{2.745 \times 10^{-4}}{1} \left( \frac{298.15}{\sqrt{33.3(132)}} \right)^{1.823} (12.8(36.4))^{1/3} (33.3(132))^{5/12} \left( \frac{1}{2.016} + \frac{1}{28.97} \right)^{1/2}$$

$$D_{\text{H}_2} = 0.792 \text{ cm}^2 \text{ s}^{-1}$$

Therefore, the VOC diffusivity is air is

$$D_{\text{MeOH}} = D_{\text{VOC}} = 0.133 \text{ cm}^2 \text{ s}^{-1}$$

Define the ratio of the diffusion area to the hole thickness  $\left( \frac{A_{\text{open}}}{x_{\text{open}}} \right)$

Drum vent bung hole dimensions (Reference 4)

Diameter of opening ~ 1 in = 2.54 cm,  $A_{\text{open}} = 5.07 \text{ cm}^2$

Thickness at bung hole  $x_{\text{open}} = 0.375 \text{ in} = 0.95 \text{ cm}$



By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling?

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Results in

$$\left( \frac{A_{\text{open}}}{x_{\text{open}}} \right)_{\text{bh}} = \frac{5.07}{0.95} = 5.34 \text{ cm}$$

Dimensions based on a self-tapping filter vent (Reference 4)

Diameter of opening = 11/16 in = 1.75cm,  $A_{\text{open}} = 2.4\text{cm}$

Thickness at bung hole  $x_{\text{open}} = 1/16 = 0.0625 \text{ in} = 0.158 \text{ cm}$

Results in

$$\left( \frac{A_{\text{open}}}{x_{\text{open}}} \right)_{\text{st}} = \frac{2.40}{0.158} = 15.2 \text{ cm}$$

The ratio  $\left( \frac{A_{\text{open}}}{x_{\text{open}}} \right)_{\text{st}} = 15.2 \text{ cm}$  is the most conservative (yields a high release rate allowing the greatest possible change in the VOC concentration in the headspace).

The total gas concentration is given by the ideal gas law

$$c = \frac{P}{RT}$$

$$c = 4.2 \text{ e} - 05 \text{ mol cm}^{-3}$$

Assuming that  $y_{\text{VOC}} = 0.001$  (1,000ppmv) (the assumed value is not important when defining relative change, [i.e., % change])

$$R_{\text{VOC,out}} = 0.001 * 0.133 * 15.2 * (4.2 \text{ e} - 05) = 8.5 \text{ e} - 08 \text{ mol s}^{-1}$$

Using Equation 2, the moles of VOC lost for a given time are

$$5.5 \text{ min (330s)} \quad N_{\text{VOC}} = (8.5 \text{ e} - 8) (330\text{s}) = 2.8\text{e} - 5 \text{ mol VOCs}$$

$$1.0 \text{ min (60s)} \quad N_{\text{VOC}} = (8.5 \text{ e} - 8) (60\text{s}) = 5.1\text{e} - 6 \text{ mol VOCs}$$

Total moles in drum headspace given by Equation 3 are

$$N_{\text{VOC,tot}} = 0.001 \frac{1 * 28,000}{82.06 * 294.3} = 0.0012 \text{ moles VOC}$$





By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling?

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Therefore, the percent loss in a given time is:

5.5 minute:	$\frac{2.8e-5}{1.2e-3} = 0.023 = 2.3\% \text{ loss}$
1.0 minute:	$\frac{5.1e-6}{1.2e-3} = 0.0042 = 0.42\% \text{ loss}$

Both of these scenarios are less than the criterion for comparability of samples that the percent relative percent difference (% RPD) be less than 25 %.

### Question 2:

How long would it take for gas sample to measure 75 % of steady state value?

Mass balance equation:

$$\frac{d(y_{\text{VOC}} N_{\text{tot}})}{dt} = -c \left( \frac{D_{\text{VOC}} A_{\text{open}}}{x_d} \right) y_{\text{VOC}}$$

Rearrange, integrate:

$$\frac{N_o}{c \left( \frac{D_{\text{VOC}} A_{\text{open}}}{x_d} \right)} \ln \left( \frac{y_f}{y_o} \right) = -t_f$$

Assume

$y_o = 0.90 y_{\text{ss}}$  90 % of steady-state value (minimum to be @ steady-state, conservative assumption)

$y_f = 0.75 y_{\text{ss}}$  75 % of steady-state value

$$c \left( \frac{D_{\text{VOC}} A_{\text{open}}}{x_d} \right) = 8.5e-5$$

$$N_o = \frac{PV}{RT} = \frac{28,000}{82.06(294.3)} = 1.16$$





By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling? Sheet No. 6 of 7  
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$$t_f = \frac{-1.16}{8.5e-5} \ln\left(\frac{0.75}{0.90}\right) = 2488 \geq 41 \text{ minutes (rounding down is conservative)}$$

**Question 3:**

How does this model calculation compare to test results from RFETS (pipe overpack)?

The results of the RFETS tests are shown in the following table (Reference 1). The %RPD is given by

$$\%RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} (100)$$

where,

$X_1$  = sample 1

$X_2$  = sample 2

Seven Tests Test	(Total VOCs) ppmv		% RPD	Total Time Filter Ventoff (s)
	Baseline Sample	Test Sample		
1	90	86	4.5	40 s
2	92	88	4.4	31 s
3	88	88	0.0	28 s
4	90	87	3.4	62 s
5	90	83.6	7.4	89 s
6	82.8	85.5	3.2	162 s
7	85.1	85.3	0.5	329 s
			Average = 3.3%	

The LLNL and RFETS the systems are similar:

- Similar packaging configuration
- DAC met before vent removal
- Short turnaround time to install a new vent

Using the model presented for Question 1 where the loss is 2.3% in 5.5 minutes and assuming an initial VOC concentration of 1000 ppm and the the final concentration is 977 ppm the %RPD is

$$\%RPD = \frac{26}{\left(\frac{1977}{2}\right)} 100 = 2.3\%$$

The model appears to be a good predictor of the expected change.



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By K. Liekhus Date 05/21/2004 Subject Does a waste drum in which the filter vent is replaced need to sit for another DAC duration before sampling? Sheet No. 7 of 7  
Chkd. By \_\_\_\_\_ Date \_\_\_\_\_ Proj. No. 844137.01.01.00.00

## Conclusions

Any VOCs removed from the drum headspace will be replaced by diffusion of VOCs from inner layers of confinement. As shown by this analysis, it is expected that there will be no statistically significant difference in measured VOC concentrations from a 55-gallon drum where a filter vent was removed and replaced over a duration no greater than 5.5 minutes. The predicted relative percent difference between before and after vent change samples is an order of magnitude less than 25% RPD typically used as a test criterion. The model prediction was comparable to test results from a similar waste configuration and sampling scenario.

It is predicted that the filter vent would have to be removed from the 55-gallon drum for a period of time of at least 41 minute before the measured VOC concentration would be less than 75% of its steady-state concentration when the filter vent is fixed on the drum lid.

## References

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